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REDUCING ATMOSPHERES: MOLECULAR ANALYSIS

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A B S T R A C T

The complex brown polymer produced on passage of an electrical discharge through a mixture of methane, ammonia, and water, is analyzed by pyrolytic GC/MS. Pyrolyzates include a wide range of alkanes, alkenes, aromatic hydrocarbons, aliphatic and aromatic nitriles, pyrroles, and pyridine. Similar pyrolyzates are obtained from polypeptides and polynucleotides with hydrocarbon moieties. This polymer is remarkably stable up to 950°C; its degradation products are candidate constituents of planetary aerosols in the outer solar system and the grains and gas in the interstellar medium.

In Miller's original experiment (1) on sparking reducing atmospheres simulating the primitive environment of the Earth, a brown solid was observed to collect on the tungsten electrodes. While α amino and hydroxy acids, and a range of other organic molecules, have been produced in this and similar experiments (2), the brown organic residue, sometimes called "intractable polymer," has proved more difficult to analyze. Yet its composition should be of substantial interest. The constituent materials of the "polymer" may be relevant to the origin of life, and a brown sludge floating on the primeval ocean may have served as radiation shielding or other environmental constraints on the earliest organisms (3). The reducing atmospheres of Jupiter, Saturn and Titan contain a blue-absorbing aerosol which may be similar to such organic polymers (4). CO and a number of other molecules are known to exist on Jupiter in strong thermodynamic disequilibrium with their low temperature environments, and are attributed to eddy diffusion from deeper and hotter atmospheric regimes (5). The dissociation of precursor molecules such as methane, ammonia, and water in the laboratory electrical discharge and the quenching of the products at much lower adjacent temperatures may simulate on a faster time scale a jovian disequilibrium convection chemistry. Interstellar grains may be produced in preplanetary stellar nebulae or in circumstellar shells and then ejected into the interstellar medium by radiation pressure or stellar winds (6). The quenching of high temperature chemical reactions in the nebula as well

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as electrical discharges in the nebula (7) have been proposed. For all these reasons, the study of arc-produced organic polymers is of some interest.

We have previously reported (8, 9) the analysis of a somewhat similar brown organic "polymer" produced by near-ultraviolet irradiation of a mixture of methane, ethane, ammonia, and water, with H_2S as the photon acceptor. The ultraviolet photoproduced polymer was found to contain 84% octatomic sulfur. The remaining 16%, analyzed after benzene extraction, appears to be a brown, sticky sludge composed of organic matter, and rich in sulfur-substituted molecules. The brown polymer produced in electrical discharge experiments described in the present paper clearly shows that elemental sulfur is not the principal cause of the absorption of these polymers at short optical wavelengths.

The experiment apparatus, displayed in Figure 1, was used to spark, with eight pairs of tungsten electrodes, an approximately equimolar mixture of methane and ammonia with a small quantity of water vapor; pre-sparking conditions were STP (10). No liquid water was introduced.

After several hours of sparking, the reaction vessel became covered with hundreds of brown spots, 1 to 2 mm in diameter, with comparable interspot spacings, somewhat resembling measles. Colors were a deep, dark brown, with no hint of yellows or reds. The spark regions were initially fairly transparent; but after several weeks of sparking a uniform film of this material completely covered the interior walls of the sparking vessel. The discharge was terminated after 35 days, at which time the interior pressure increment was 0.3 atmospheres larger than at 0 hours. No substantial variation in pressure occurred when cold fingers on the main flask and sparking vessel were brought to liquid N₂ temperatures, indicating evolution of such gases as H₂, N₂, and CO. The large-scale production of CO and N₂ in such experiments is of interest for the chemistry of reducing planetary atmospheres and will be discussed elsewhere. At the end of the experiment all gases were pumped out, the reaction vessel opened and the brown polymer subjected to a range of analyses, including mass spectroscopy, combined gas chromatography and mass spectroscopy (GC/MS), and thermogravimetric analysis (11).

Low sensitivity direct insertion mass spectrometry showed as principal pyrolysis products H₂, CO₂, HCN, CH₃CN, and CH₃CHO. These nitriles and aldehydes had originally been detected on the gas phase of the original experiment by Sagan and Miller (12). The pyrolytic GC/MS approach improves the detection sensitivity over direct probe insertion

by a factor of $> 10^6$, and is the method of choice when, as in the present case, the material has a very low vapor pressure and resists standard derivatization procedures. Although the pyrolyzate was separated by GC prior to MS, analysis of individual GC peaks indicates many are mixtures of two or more compounds, as has been found for complex soluble products in previous experiments on pre-biological organic chemistry. The identifications reported here are based both on the principal MS peaks and on the GC retention times. There is a tendency for polar compounds to be absorbed in the analytic system and produce spectral overlap. We have also confirmed some 75% of the pyrolysis products by the ADP computer search system.

The compounds released at various temperatures during the sequential vacuum pyrolyses are given in Table 1. This table indicates that some, but not all, of the nitrogen-containing compounds released at 150° and 300°C, such as acetonitrile, acrylonitrile, and benzonitrile are less tightly bound in the polymer than the majority of hydrocarbons which were not released until 450°C. Also, there is a dearth of oxygen compounds; yet CO₂ is a major product at all pyrolysis temperatures, perhaps indicative of carboxylic acids. It is interesting to note that acetic acid, the only oxygen compound besides CO₂, was released only at 150°C and, therefore, could not possibly be a pyrolysis artifact. The persistence of the same

pyrolysis products at increasing pyrolysis temperatures serves as an experimental confirmation that secondary reactions during high temperature pyrolyses were of minimal importance.

The non-sequential pyrolysis at 600°C is given in Table 2. As this pyrolysis was conducted with a larger quantity of polymer and at the maximum temperature available to us, it confirmed the sequential pyrolysis results and helped to identify a greater and more diverse suite of components. As in the pyrolysis of U.V. photoproduct "polymer," published earlier (9), we again obtained, by both types of pyrolyses, series of homologous compounds typical of abiological syntheses. The various results suggest that the spark-discharge "polymer" has a relatively stable matrix which consists, at least in part, of nitrogenous compounds, and probably also of hydrocarbons. Additional nitrogenous components are attached to this matrix through highly varied bonding energies.

The pyrolyzate of the brown polymer produced in our H₂S ultraviolet experiment (9) contained alkanes, alkenes and alkyl disulphides up to C₇. A rather similar list of saturated and unsaturated aliphatic hydrocarbons up to C₇ are found in the present spark discharge experiment. Simple and substituted aromatic hydrocarbons are found in both experiments. Thiophenes, mercaptans,

disulphides, and C = S compounds found in the ultraviolet experiment are, of course, not present in the spark discharge experiment. The variety and nature of the nitrogenous compounds found in the spark experiments is striking. More than 15 nitriles are identified.

The pyrolyzates of the spark-discharge polymer consist mostly of aliphatic and aromatic nitriles, pyrrole, short chain ($\leq C_4$) aliphatic hydrocarbons with minor amounts of aromatic hydrocarbons. The above suite of pyrolysis products can be derived from the pyrolysis of a polymer consisting basically of amino acids and/or polypeptides (13). However, other nitrogen containing polymers, including polynucleotides, also give rise to nitriles upon pyrolysis, and the hydrocarbon pyrolyzates could be breakdown products of a methanogenous polymer. Therefore, the polymer formed during this spark-discharge reaction between CH_4 , NH_3 , and H_2O could be largely a heteropolypeptide formed from $HCN-H_2O$ polymerization (14), or a nitrile polymer (2), each likely containing some hydrocarbon moieties, or a combination of both. The pyrolyzates listed in Tables 1 and 2 are similar to the pyrolysis fragments from polypeptides, polynucleotides, and hydrocarbon polymers, and are therefore of some interest in the context of the origin of life. The presence of pyrroles is also noteworthy.

Thermogravimetric analyses for both the ultraviolet sulfur-rich brown "polymer" (9) and the electric discharge sulfur-free brown "polymer" are shown in Figure 2. The weight loss derivative near 200°C was so steep for the ultraviolet polymer that the experiment was terminated at that temperature for fear of contaminating the thermogravimetric analyzer. The discharge "polymer," on the other hand, exhibits remarkable thermal stability, being only half-dissociated at 950°C. Brown polymeric material of the sort described in this experiment, therefore, can plausibly have been ejected from high temperature circumstellar clouds during the Hayashi phase of early stellar evolution or after the red giant stage of late stellar evolution and survived to interstellar space. The infrared absorption, spallation products, and other properties of this material seem to match astronomical observations of the interstellar medium; and we propose that the polymer described in this paper may be quite similar to a principal constituent of the interstellar grains (16).

We have here reported only the pyrolyzates of the brown polymer, not its full structure which must be extremely complex. However, thermal and radiation degradation of the polymer is likely to make some of the molecules reported in Tables 1 and 2 accessible, both in the atmospheres of Jupiter, Saturn and Titan, and in the

interstellar medium to appropriate spectral analysis. Temperatures of 950°C are reached on Jupiter at pressures of hundreds of bars; the characteristic circulation time to the 1 to 0.1 bar level, where spectroscopic observations can be made, is roughly a year (4). If such a polymer exists on Jupiter its high vapor pressure pyrolysis products should be circulated to the highest atmosphere where they may be subject to spectroscopic or direct entry probe identification.

References and Notes

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10. In a typical experiment, a pyrex flask, shown at right in Figure 1, is connected to the sparking vessel with a combined total volume of 13.326 liters and filled with methane, ammonia, and water vapor at respective volume mixing ratios of 51.3 ± 3.0 , 45.9 ± 3.6 , and $2.6 \pm 0.8\%$. The gases were transferred by a three-stage mercury diffusion pump in tandem with a mechanical pump, capable of producing a vacuum less than 10^{-6} torr. Matheson anhydrous ammonia and research purity methane, both at 99.99% minimum purity were separately purified further by low temperature vacuum distillation, down to -196°C , until found tensometrically homogeneous. Comparable precautions were taken with distilled water. Methane and ammonia were initially transferred into the sparking vessel through a low temperature spiral trap. Teflon stopcocks were used. The high frequency Tesla coils employed

are BD-20 and BD-10 made by Electro-technic Products, Chicago, Illinois, supplying approximately 50 Kv at 4 to 5 MHz, and 50 Kv at 3 to 5 MHz, respectively. Spark length for the 8 pairs of electrodes was approximately 1/4 inch; they were operated according to a sequential program, no adjacent coils operating at the same time.

11. High vacuum pyrolysis was carried out on a 25 mg sample of the polymer which had been degassed at high vacuum and room temperature to remove most of the absorbed gases. The products were trapped at liquid N₂ temperatures and then injected directly into a GC which in turn was directly connected through a heated transfer line to the MS system. The polymer product, now pyrolyzed at 150°C was then returned to room temperature, heated to 300°C, its pyrolysis products trapped at liquid N₂ temperatures, and then again directly transferred to the GC/MS system. Such sequential pyrolysis was continued at 450°C and 600°C; and 50 mg of sample "polymer" subjected to a single high temperature pyrolysis at 600°C as well. The analysis of the pyrolysis products was achieved using a Perkin-Elmer Model 226 GC equipped with a 150' x 0.02" id OS 138-polyphenylether/SCOT capillary column. The GC was programmed from 40 to 190°C at 2-5°C min⁻¹ after an initial 10 min. period at 40°C. The gas chromatograph was interfaced to a Hitachi RMU-6E medium resolution mass spectrometer through a Watson-Biemann molecular separator. Five-second mass scans were taken of each peak as it emerged from the gas chromatograph. Details of the pyrolysis apparatus are described by E.L. Bandurski and B. Nagy [Geochim. Cosmochim. Acta, 40, 1397 (1976)]. The polymer was also studied less sensitively in the temperature range 22 to 500°C on an AEI MS-902 double focusing MS using a direct insertion probe.
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17. This research was supported by NASA Grant NGR 33-010-101. We are indebted to Robert Weaver for thermogravimetric analysis and to Eric Bandurski for assistance during the mass spectrometric scans.

Table 1

"Polymer" Components from Spark-Discharged Synthesis Experiments

(CH₄, NH₃, H₂O Mixture)**

Sequential Pyrolyses at 150°, 300°, 450° and 600° C

(~ 25 mg of "polymer" pyrolyzed)

COMPOUNDS IDENTIFIED	*	MW	COMPOUNDS IDENTIFIED	*	MW
<u>150°C</u>			<u>450°C</u>		
carbon dioxide	M	44	carbon dioxide	M	44
hydrogen cyanide	M	27	hydrogen cyanide	M	27
ammonia	M	17	ammonia	M	17
butadiene	m	54	ethane	M	30
acetic acid	m	60	butane	m	58
acetonitrile	M	41	pentane	m	72
acrylonitrile	M	53	butene	M	56
succinonitrile	m	80	pentene	m	70
benzonitrile	m	103	toluene	m	92
			xylene	m	106
<u>300°C</u>			C ₃ -alkylbenzene	m	120
carbon dioxide	M	44	C ₂ -alkylindane	m,t	146
hydrogen cyanide	M	27	methylinene	m,t	130
ammonia	M	17	acetonitrile	M	41
ethane	M	30	propanenitrile	M	55
propene	M	42	pentanenitrile	m	83
butene	m	56	acrylonitrile	M	53
acetonitrile	M	41	succinonitrile	m	80
propanenitrile	M	55	benzonitrile	m	103
acrylonitrile	m	53	tolunitrile	m	117
succinonitrile	m	80	indole	m,t	117
benzonitrile	m	103			
			<u>600°C</u>		
			carbon dioxide	M	44
			hydrogen cyanide	M	27
			ammonia	M	17
			ethane	M	30
			acetonitrile	M	41
			acrylonitrile	m	53
			benzonitrile	m	103

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*M = major component, m = minor component, t - tentative identification

**CH₄ = 49.0% NH₃ = 48.5% H₂O = 2.5%

Table 2

"Polymer" Components from Spark-Discharge Synthesis Experiments

(CH₄, NH₃, H₂O Mixture)**

Non-sequential Pyrolysis at 600° C

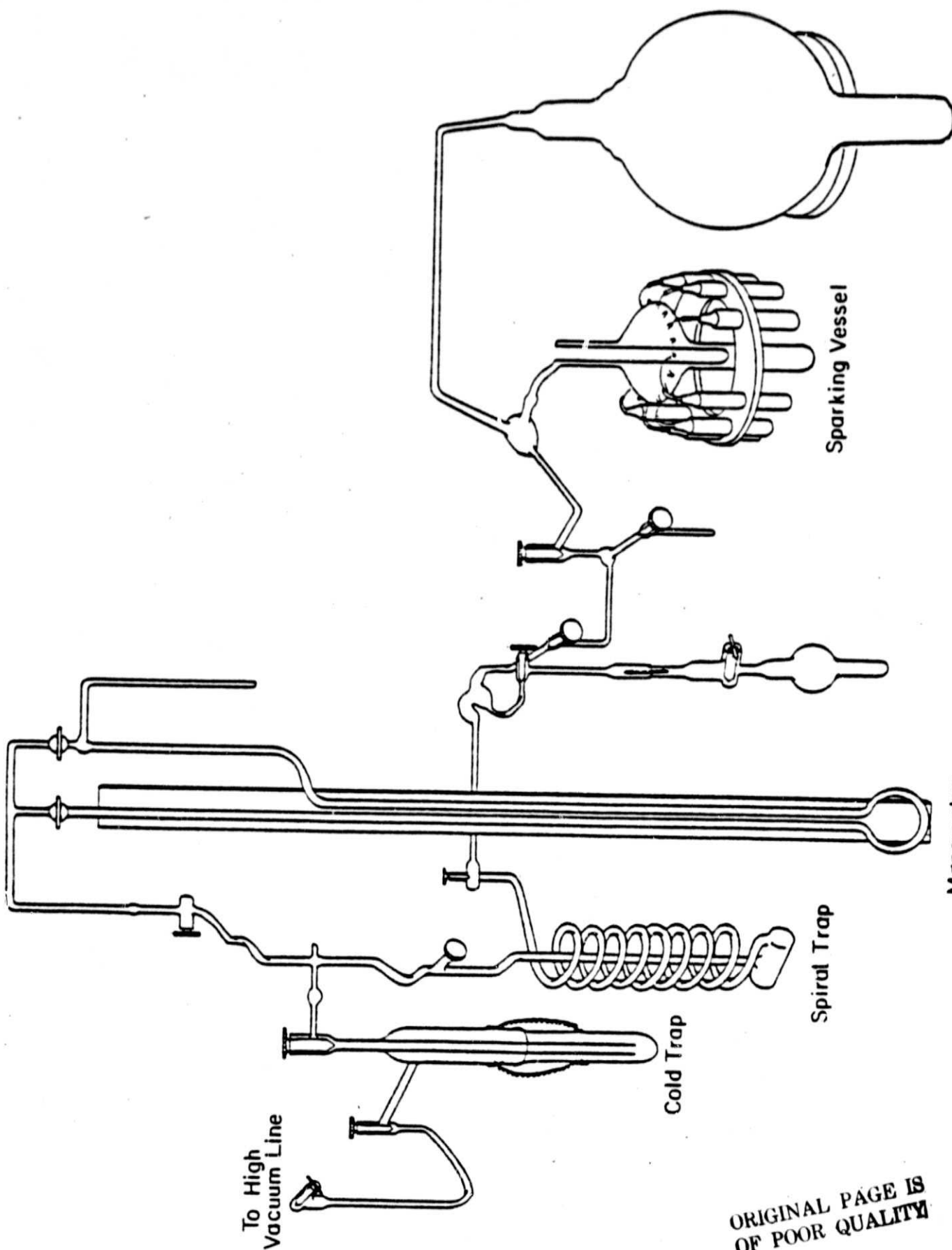
(50 mg of "polymer" pyrolyzed)

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COMPOUNDS IDENTIFIED	*	MW	COMPOUNDS IDENTIFIED	*	MW
carbon dioxide	M	44	<u>Nitrogenous Compounds</u>		
<u>Hydrocarbons</u>			hydrogen cyanide	M	27
ethane	M	30	ammonia	M	17
propane	M	44	acetonitrile	M	41
butane	M	58	propanenitrile	M	55
ethene	M	28	2-methylpropanenitrile	M	69
propene	M	42	butanenitrile	M	69
butene	M	56	pentanenitrile	M	83
C ₅ -alkene	m	70	C ₆ -alkylnitrile	m, t	97
butadiene	m	54	acrylonitrile	m	53
C ₇ -diunsaturated			butenenitrile or		
hydrocarbon	m	96	methacrylonitrile	M	67
tolune	m	92	pentenenitrile	m	81
ethylbenzene	m	106	succinonitrile	M	80
xylene	m	106	glutaronitrile	M	94
trimethylbenzene	m	120	N, N-dimethylamino-		
C ₄ -alkylbenzene	m	134	ethanenitrile	m	84
indane or methyl-			benzonitrile	m	103
styrene	m	118	tolunitriles	M	117
indene	m	116	pyrrole	M	67
methylindene	m	130	pyridine	m	79
naphthalene	m	128	methylpyridine	m	93
			C ₂ -alkylpyridines	m	107
			methylethylpyrazine	m, t	122

*M = major component, m = minor component, t = tentative identification

**CH₄ = 49.0%NH₃ = 48.5%H₂O = 2.5%



Manometer
Figure 1

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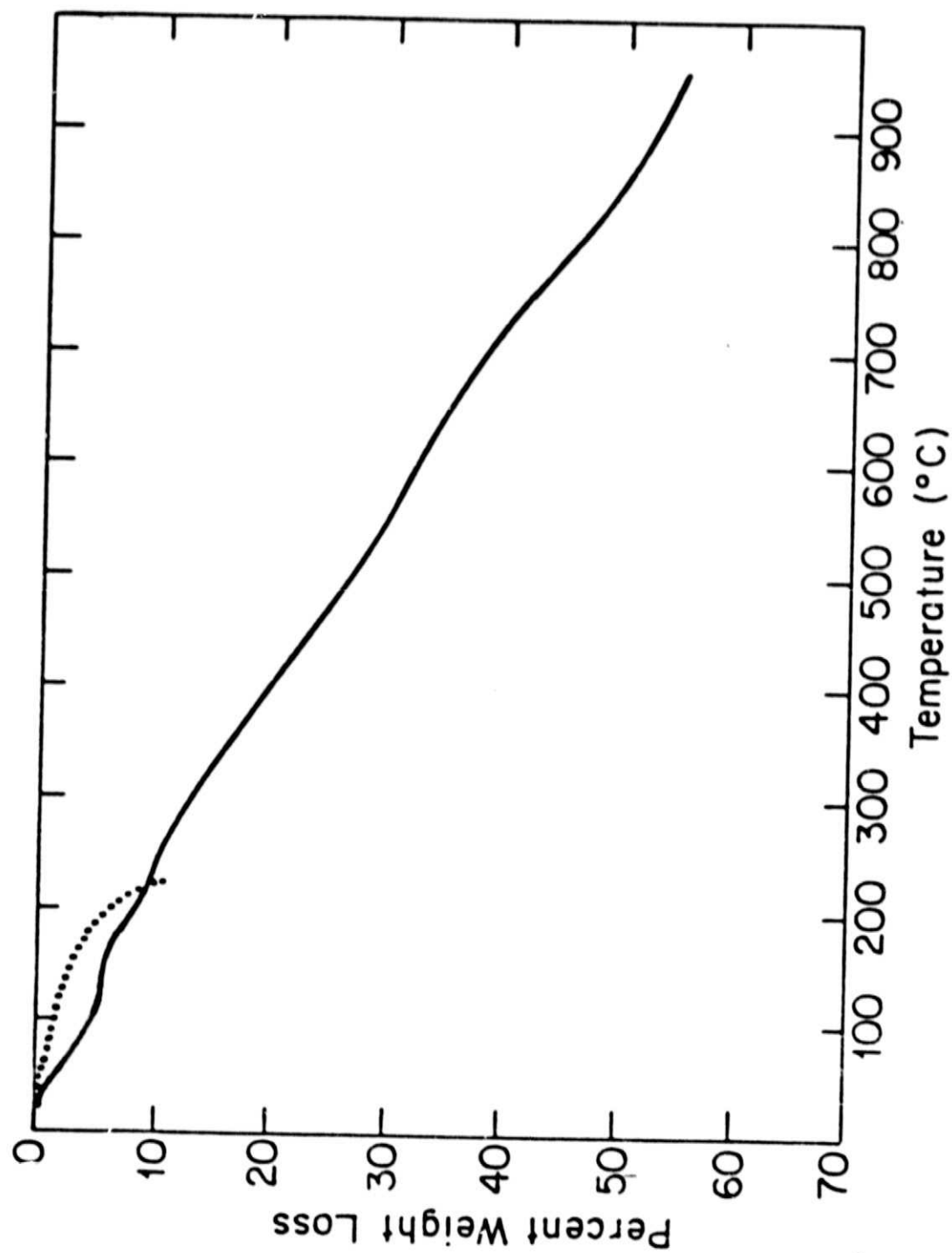


Figure 2. Thermogravimetric analysis of (i) dark brown polymeric material produced by electric spark through CH_4 , NH_3 , and H_2O (vapor), solid line; and (ii) sulfur free brown polymeric material produced by photolysis of CH_4 , C_2H_6 , NH_3 , H_2O and H_2S , dotted line. The curves show weight loss of material versus temperature.